

**Mathematical modeling of semiconductors:
From quantum mechanics to devices**

Markus Kantner, Alexander Mielke, Markus Mittnenzweig, Nella Rotundo

submitted: February 19, 2019

Weierstrass Institute
Mohrenstr. 39
10117 Berlin
Germany
E-Mail: markus.kantner@wias-berlin.de
alexander.mielke@wias-berlin.de
nella.rotundo@wias-berlin.de

No. 2575
Berlin 2019



2010 *Mathematics Subject Classification.* 35K57, 80M30, 81S22, 82D37.

Key words and phrases. Semiconductor modeling, drift-diffusion system, open quantum system, Lindblad operator, reaction-diffusion systems, detailed balance condition, gradient structure, thermodynamically consistent coupling.

The research was partially supported by the ERC grant AdG 267802 (AnaMultiScale) and the German Research Foundation (DFG) via project B4 within the collaborative research center SFB 787 *Semiconductor Nanophotonics*. The authors are grateful for helpful and stimulating discussions with Uwe Bandelow and Thomas Koprucki.

Edited by
Weierstraß-Institut für Angewandte Analysis und Stochastik (WIAS)
Leibniz-Institut im Forschungsverbund Berlin e. V.
Mohrenstraße 39
10117 Berlin
Germany

Fax: +49 30 20372-303
E-Mail: preprint@wias-berlin.de
World Wide Web: <http://www.wias-berlin.de/>

Mathematical modeling of semiconductors: From quantum mechanics to devices

Markus Kantner, Alexander Mielke, Markus Mittnenzweig, Nella Rotundo

Abstract

We discuss recent progress in the mathematical modeling of semiconductor devices. The central result of this paper is a combined quantum-classical model that self-consistently couples van Roosbroeck's drift-diffusion system for classical charge transport with a Lindblad-type quantum master equation. The coupling is shown to obey fundamental principles of non-equilibrium thermodynamics. The appealing thermodynamic properties are shown to arise from the underlying mathematical structure of a damped Hamiltonian system, which is an isothermal version of so-called GENERIC systems. The evolution is governed by a Hamiltonian part and a gradient part involving a Poisson operator and an Onsager operator as geometric structures, respectively. Both parts are driven by the conjugate forces given in terms of the derivatives of a suitable free energy.

1 Introduction

The development of semiconductor devices has been strongly supported by mathematical modeling and numerical simulations over the last decades. Mathematical models provide insights into the internal physical mechanisms in semiconductor devices, can help to optimize particular designs and decrease the development costs by reducing the demand for the expensive processing of a large number of prototypes. For instance, the progress in performance and miniaturization of silicon transistors following Moore's law over the last decades was inconceivable without modern TCAD (technology computer-aided design) simulation tools. The on-going reduction of the characteristic length scales of semiconductor devices as well as the integration of semiconductor nanostructures such as quantum dots [2], requires an extension of the classical semiconductor device equations towards the inclusion of quantum mechanical models.

Many modern opto-electronic devices such as, e.g., quantum light sources and nanolasers [6], employ semiconductor quantum dots as an optically active element embedded in photonic micro-resonators. The transport of charge carriers in such devices can be described by semi-classical drift-diffusion-reaction models, such as the van Roosbroeck system [38]. For example, in [13] the current injection into an electrically driven single-photon emitting diode has been investigated in order to understand the experimentally observed malfunction of the design, see Fig. 1. The device features an oxide aperture that is intended to confine the injection current into a narrow region above the aperture, where a single quantum dot shall be electrically excited. The experimentally observed electroluminescence, however, indicates a counterintuitive rapid lateral current spreading. On the basis of the van Roosbroeck system, the phenomenon was reproduced in numerical simulations and eventually understood as an inherent feature of the design under the typical operation conditions of the device. Finally, based on mathematical modeling, a revised design with superior current confinement was suggested [13]. While this example convincingly substantiates the importance of carrier transport modeling, many other important properties of the single-photon source can not be described by the van Roosbroeck system. In particular, the quantum optical features of the radiation generated by the quantum dot, namely the correlation statistics of the emitted photons that allow to quantify non-classical

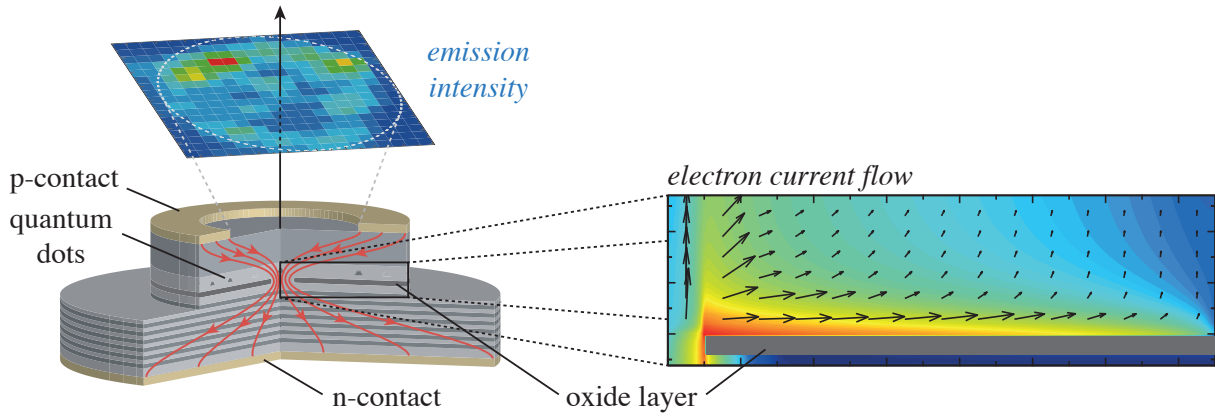


Figure 1: Lateral current spreading in an oxide-confined single-photon source leading to unwanted optical activity of parasitic quantum dots in the outer parts of the structure [13].

phenomena like “photon anti-bunching” [37], are not accessible by the van Roosbroeck system. This requires a microscopic modeling framework, that describes the evolution of open quantum systems.

A broad class of problems in semiconductor quantum optics can be described by quantum master equations [4]. These are evolution equations for the quantum mechanical density matrix $\rho \in \mathbb{C}^{n \times n}$, that is an Hermitian operator which describes the state of a quantum system. Unlike the Schrödinger equation, which models the Hamiltonian evolution of closed quantum systems, quantum master equations allow for the consideration of dissipative dynamics that arise due to the coupling of the quantum system with its macroscopic environment. The simplest class of quantum master equation, which guarantees the preservation of trace $\text{tr} \rho = 1$, self-adjointness $\rho = \rho^*$, and positivity $\rho \geq 0$ of the density matrix, is the Lindblad master equation [18, 19], see (29). While providing access to the microscopic dynamics and the quantum optical figures of merit of open quantum systems, the Lindblad equation (1d) complements the classical modeling approaches to semiconductor devices based on the van Roosbroeck system for the electrostatic potential ϕ and the charge carrier densities n and p for electrons and holes, respectively.

Our interest lies in a mathematically systematic and thermodynamically correct derivation of coupled systems of the form

$$0 = \text{div}(\varepsilon \nabla \phi) + e_0(C + p - n + \rho_{\text{qd}} \text{tr}(Z\rho)), \quad (1a)$$

$$\dot{n} = \text{div}(\mathbb{M}_n(\nabla n - n \nabla \phi)) - R(n, p) + R_n^{\text{quant-class}}(n, p, \rho), \quad (1b)$$

$$\dot{p} = \text{div}(\mathbb{M}_p(\nabla p + p \nabla \phi)) - R(n, p) + R_p^{\text{quant-class}}(n, p, \rho), \quad (1c)$$

$$\dot{\rho} = \mathcal{J}[\rho, H + e_0 \phi Z] + \mathfrak{D}_0 \rho + \mathfrak{D}(n, p) \rho. \quad (1d)$$

In [14], a hybrid quantum-classical modeling approach was introduced that self-consistently combines these two approaches and allows for a comprehensive description of quantum dot-based semiconductor devices for quantum optical applications. Here we want to show that this model is a special case of a general class of models that have the form of damped Hamiltonian system, in the sense explained now.

From a mathematical point of view the thermodynamic consistency of complex physical systems like (1) can be encoded in the GENERIC framework. GENERIC is an acronym for *General Equations for Non-Equilibrium Reversible Irreversible Coupling* and provides a thermodynamically consistent way of coupling reversible Hamiltonian dynamics with irreversible dissipative

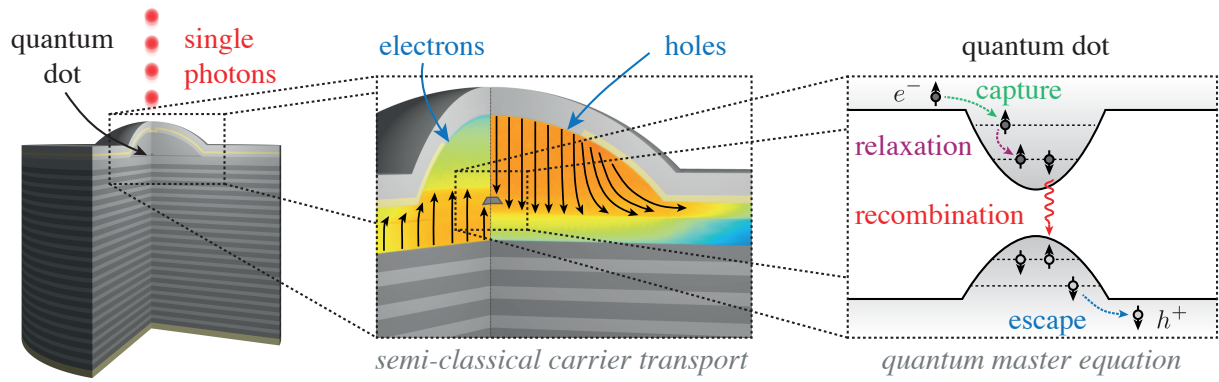


Figure 2: The hybrid quantum-classical modeling approach for quantum light sources combines semi-classical carrier transport theory with microscopic models for the quantum dot-photon system [12].

dynamics, see [9, 35] and Section 3.1. In Section 3.2 we introduce the concept of *damped Hamiltonian systems* as a simplified, isothermal version of GENERIC systems. They are defined by a quadruple $(\mathcal{Q}, \mathcal{F}, \mathbb{J}, \mathbb{K})$ where \mathcal{Q} is the state space and $\mathcal{F}(q)$ is the free energy functional on it. Moreover, the state space carries two geometric structures, namely the Poisson structure \mathbb{J} that generates the Hamiltonian evolution and the Onsager operator \mathbb{K} driving the dissipative dynamics. The time evolution of the damped Hamiltonian system $(\mathcal{Q}, \mathcal{F}, \mathbb{J}, \mathbb{K})$ is given via

$$\dot{q} = (\mathbb{J}(q) - \mathbb{K}(q))D\mathcal{F}(q). \quad (2)$$

The Poisson operator $\mathbb{J}(q)$ is skew-symmetric and satisfies the Jacobi identity, while the Onsager operator $\mathbb{K}(q)$ is symmetric and positive semidefinite, which encodes the second law of thermodynamics.

The aim of the paper is to realize (1) in the form (2) with the state variable by $q = (n, p, \rho)$. For this, we first introduce in details the van Roosbroeck system (1), but without (1d), in Section 2. Next, we shortly summarize the abstract, thermodynamical modeling via the GENERIC framework in Section 3.1 and via so-called *damped Hamiltonian systems* in Section 3.2. A special emphasis to the additive structure of dissipative processes and to admissible couplings are given in Sections 3.3 and 3.4, respectively.

In Section 4 we then apply the abstract theory to (1), first to certain subparts and finally to the full coupled system. Based on [1] it was shown in [23] that the van Roosbroeck system for (ϕ, n, p) can be written as a gradient system (i.e. with $\mathbb{J} \equiv 0$), see Section 4.2. Extensions to more general reaction systems or to more general carrier statistics are discussed next. The most recent building block of the theory was provided in [29], where it was shown that all Markovian quantum master equation in Lindblad form that satisfy a suitable detailed-balance condition can be written as a damped Hamiltonian, see Section 4.5. In Section 4.6, we present the analysis from [14] which allows to show that the free energy is a Liapunov function, without referring to Onsager operator. Finally, Section 4.7 contains the nontrivial coupling between quantum and classical system via Onsager operators.

The ideas in this paper provide a series of mathematical concepts that are useful in modeling complex physical system, where different components interact in nontrivial ways. Here, we apply these concepts to models for semiconductor physics, but we believe that they are also relevant and helpful many other application areas.

2 The van Roosbroeck system

The van Roosbroeck system is a system of drift-diffusion-reaction equations that describe the transport of charge carriers in semiconductor devices in their self-consistently generated electrostatic field. The model equations are posed on a domain $\Omega \in \mathbb{R}^d$ with $d = 1, 2$ or 3 , time $t \in [0, T]$ and read

$$0 = \operatorname{div}(\varepsilon \nabla \phi) + e_0(C + p - n), \quad (3a)$$

$$\dot{n} = -\operatorname{div} \mathbf{J}_n - R(n, p), \quad (3b)$$

$$\dot{p} = -\operatorname{div} \mathbf{J}_p - R(n, p). \quad (3c)$$

The continuity equations (3b)–(3c) model the transport and recombination dynamics of the electron density n and hole density p , where \mathbf{J}_n and \mathbf{J}_p are the respective carrier flux densities. The reaction rate R describes the recombination and generation kinetics of electron-hole pairs, which can be created or annihilated in several radiative and non-radiative processes [40, 20]. The electrostatic interaction between the negatively charged electrons and the positively charged holes (which are missing electrons), is mediated by Poisson's equation (3a) for the electrostatic potential ϕ . Here, e_0 is the elementary charge, ε is the dielectric permittivity of the semiconductor material and $C : \Omega \rightarrow \mathbb{R}$ is the built-in doping profile.

2.1 Carrier flux densities and chemical potentials

The van Roosbroeck system needs to be supplemented by state equations for the carrier densities and the carrier flux densities. The drift-diffusion flux densities read

$$\mathbf{J}_n = \mathbb{M}_n n \nabla \phi - \mathbb{D}_n \nabla n, \quad \mathbf{J}_p = -\mathbb{M}_p p \nabla \phi - \mathbb{D}_p \nabla p, \quad (4)$$

where the gradient of the electrostatic potential generates the drift transport of the charge carriers within the electric field $\mathbf{E} = -\nabla \phi$. As the charges of electrons and holes have different signs, they drift into opposite directions. The electric conductivity is determined by the carrier mobilities \mathbb{M}_n and \mathbb{M}_p that are material-dependent parameters. A second process leading to the transport of charge carriers is diffusion, which is driven by the gradients of the carrier densities. In the simplest case the diffusion constant matrices \mathbb{D}_n and \mathbb{D}_p are linked to the mobility matrices via the Einstein relation

$$\mathbb{D}_n = \frac{k_B \theta}{e_0} \mathbb{M}_n, \quad \mathbb{D}_p = \frac{k_B \theta}{e_0} \mathbb{M}_p, \quad (5)$$

which is a manifestation of the fluctuation-dissipation theorem. Here, k_B is the Boltzmann constant and θ is the temperature.

The carrier densities are linked to the electrostatic potential ϕ and the electro-chemical potentials μ_n and μ_p , often denoted also as *quasi-Fermi energies*, by the state equations

$$n = N_n \mathfrak{F} \left(\frac{\mu_n - (E_n - e_0 \phi)}{k_B \theta} \right), \quad p = N_p \mathfrak{F} \left(\frac{\mu_p - (E_p + e_0 \phi)}{k_B \theta} \right). \quad (6)$$

The equations for the carrier densities (6) are based on the assumption of a quasi-equilibrium distribution of the electrons and holes in the material. The function \mathfrak{F} contains information on

the statistical distribution function underlying the nature of the particles (Fermi–Dirac statistics for fermions, Bose–Einstein statistics for bosons or Maxwell–Boltzmann statistics for classical particles), the energy band structure and the density of states provided by the material. The effective density of states N_n , N_p and the band-edge energy levels E_n , E_p are material specific parameters. Throughout this work we focus on the most simple case of non-degenerate semiconductors in which the Maxwell–Boltzmann statistics is considered, this means that $\mathfrak{F}(x) = \exp(x)$ is an exponential function. At high carrier densities or at cryogenic temperatures, degeneration effects due to the Pauli exclusion principle come into play. In this case \mathfrak{F} is typically given by a Fermi–Dirac integral in conventional semiconductor crystals [40], or the Gauss–Fermi integral in disordered organic materials [21]. As a consequence, the Einstein relation (5) must be generalized in degenerate semiconductors to account for the density-dependent nonlinear diffusion [15, 21].

Using the Einstein relation (5) and considering the Maxwell–Boltzmann statistics in the state equations (6), the flux densities can be written as gradients of the chemical potentials

$$\mathbf{J}_n = -\frac{1}{e_0} \mathbb{M}_n n \nabla \mu_n, \quad \mathbf{J}_p = -\frac{1}{e_0} \mathbb{M}_p p \nabla \mu_p. \quad (7)$$

This reflects a basic principle of linear irreversible thermodynamics, where the gradients of the chemical potentials are the thermodynamic forces driving the carrier flux [31, 10].

In the thermodynamic equilibrium, the chemical potentials approach a common global constant $\mu_n^{\text{eq}} \equiv \mu_p^{\text{eq}} \equiv 0$ such that the net current flow vanishes. Microscopically, this feature emerges from the principle of detailed balance principle in the thermodynamic equilibrium. The corresponding equilibrium carrier densities of the non-degenerate semiconductor read

$$n_{\text{eq}} = N_n \exp\left(-\frac{E_n - e_0 \phi_{\text{eq}}}{k_B \theta}\right), \quad p_{\text{eq}} = N_p \exp\left(-\frac{E_p + e_0 \phi_{\text{eq}}}{k_B \theta}\right), \quad (8)$$

where ϕ_{eq} solves (3a) with equilibrium boundary conditions (see Section 2.2). Finally, the reaction rate R takes the form

$$R(n, p) = r(n, p) (np - n_{\text{eq}} p_{\text{eq}}), \quad (9)$$

with $r(n, p) = \sum_{m=1}^{m_*} r_m(n, p) \geq 0$, where $m = 1, \dots, m_*$ labels various recombination processes (e.g, Shockley–Read–Hall recombination, direct band-to-band recombination, Auger recombination etc., see [40, 36]). For the bi-polar van Roosbroeck system with non-degenerate carrier statistics one often introduces the intrinsic carrier density n_{intr} according to $n_{\text{intr}}^2 = n_{\text{eq}} p_{\text{eq}}$.

2.2 Boundary conditions

The van Roosbroeck system (3) is supplemented with initial conditions at time $t = 0$

$$\phi(x, 0) = \phi^I(x), \quad \mu_n(x, 0) = \mu_n^I(x), \quad \mu_p(x, 0) = \mu_p^I(x) \quad \text{for } x \in \Omega,$$

where ϕ^I , μ_n^I and μ_p^I are the initial distributions.

Regarding the boundary conditions modeling electrical contacts or semiconductor-insulator interfaces, we assume a decomposition of the domain boundary as

$$\partial\Omega = \Gamma_D \cup \Gamma_N,$$

with Dirichlet boundary conditions imposed on Γ_D and Neumann conditions on Γ_N . Ideal Ohmic contacts are modeled as Dirichlet boundary conditions. For a device featuring several Ohmic contacts $\Gamma_D = \bigcup_\alpha \Gamma_{D,\alpha}$, one imposes

$$\phi(x, t) = \phi_0(x) + U_\alpha(t), \quad \mu_n(x, t) = -e_0 U_\alpha(t), \quad \mu_p(x, t) = e_0 U_\alpha(t) \quad (10)$$

for all $x \in \Gamma_{D,\alpha}$. Here, $U_\alpha(t)$ is the (possibly time-dependent) voltage applied to the α -th contact and $\phi_0(x)$ is the built-in electrostatic potential that enforces local charge neutrality on $\Gamma_{D,\alpha}$, i.e., it holds

$$0 = C + N_p \mathfrak{F} \left(\frac{-E_p - e_0 \phi_0}{k_B \theta} \right) - N_n \mathfrak{F} \left(\frac{-E_n + e_0 \phi_0}{k_B \theta} \right)$$

everywhere on Γ_D . In the case of Maxwell–Boltzmann statistics, the built-in potential can be explicitly obtained as

$$\phi_0 = -\frac{E_p - E_n}{2e_0} + \frac{k_B \theta}{2e_0} \log \left(\frac{N_p}{N_n} \right) + \frac{k_B \theta}{e_0} \operatorname{arsinh} \left(\frac{C}{2n_{\text{intr}}} \right).$$

For degenerate semiconductors ϕ_0 must be obtained numerically. See [39, 36, 40] for other boundary conditions modeling electrical contacts, e.g., Gate contacts or Schottky contacts. On the boundary segments Γ_N one typically imposes no-flux boundary conditions

$$\boldsymbol{\nu} \cdot \nabla \phi = 0, \quad \boldsymbol{\nu} \cdot \mathbf{J}_n = 0, \quad \boldsymbol{\nu} \cdot \mathbf{J}_p = 0, \quad (11)$$

which are homogeneous Neumann boundary conditions that guarantee that the computational domain is self contained. Here, $\boldsymbol{\nu}$ is the outward-oriented normal vector on the boundary segment. The boundary conditions (11) are no physical boundaries and must be chosen carefully in order to restrict the computational domain to a reasonably small region [39].

3 Mathematical modeling based on thermodynamical principles

The classical approach to thermodynamical modeling starts from balance laws (e.g., for mass of different species, linear momentum, charges, energy, etc.) and then adds suitable constitutive relations to connect the state variables and the fluxes. In a second step, the constitutive laws are restricted to satisfy the second law of thermodynamics, i.e., the entropy is non-decreasing in non-isothermal systems. Correspondingly for systems at constant temperature the total energy is not conserved, but a suitable free energy is decreasing.

Here we will use a different approach that starts from energy and entropy functionals and uses their derivatives with respect to the state variables (also called thermodynamical conjugate forces) as driving forces. We first discuss the more general modeling framework GENERIC and then restrict to the isothermal version, which we refer to as *damped Hamiltonian systems*.

3.1 The GENERIC framework

The framework of GENERIC was introduced by Morrison [30] under the name *metriplectic systems*, see [3, Sec. 15.4] for an outline of these early developments. In [9, 35] Öttinger and

Grmela introduced the name GENERIC to emphasize the thermodynamical modeling aspects that were relevant for their applications in fluid mechanics. More mathematical formulations are given in [22, 25] with applications to thermoplasticity and optoelectronics, respectively.

A GENERIC system is a quintuple $(\mathcal{Q}, \mathcal{E}, \mathcal{S}, \widehat{\mathbb{J}}, \widehat{\mathbb{K}})$, where the smooth functionals \mathcal{E} and \mathcal{S} on the state space \mathcal{Q} denote the total energy and the total entropy, respectively. Moreover, \mathcal{Q} carries two geometric structures, namely a Poisson structure $\widehat{\mathbb{J}}$ and a dissipative Onsager structure $\widehat{\mathbb{K}}$, i.e., for each $q \in \mathcal{Q}$ the operators $\widehat{\mathbb{J}}(q)$ and $\widehat{\mathbb{K}}(q)$ map the cotangent space $T_q^*\mathcal{Q}$ into the tangent space $T_q\mathcal{Q}$. The evolution of the system is given as the sum of the Hamiltonian part $\widehat{\mathbb{J}}(q)D\mathcal{E}(q)$ and the gradient-flow $\widehat{\mathbb{K}}(q)D\mathcal{S}(q)$, namely

$$\dot{q} = \widehat{\mathbb{J}}(q)D\mathcal{E}(q) + \widehat{\mathbb{K}}(q)D\mathcal{S}(q). \quad (12)$$

The basic conditions on the geometric structures $\widehat{\mathbb{J}}$ and $\widehat{\mathbb{K}}$ are the symmetries

$$\widehat{\mathbb{J}}(q) = -\widehat{\mathbb{J}}^*(q) \quad \text{and} \quad \widehat{\mathbb{K}}(q) = \widehat{\mathbb{K}}^*(q) \quad (13)$$

and the structural properties

$$\begin{aligned} \widehat{\mathbb{J}} \text{ satisfies Jacobi's identity,} \\ \widehat{\mathbb{K}}(q) \text{ is positive semi-definite, i.e., } \langle \xi, \widehat{\mathbb{K}}(q)\xi \rangle \geq 0. \end{aligned} \quad (14)$$

Here, Jacobi's identity for $\widehat{\mathbb{J}}$ holds, if for all $\eta_j \in T_q^*\mathcal{Q}$ we have

$$\langle \eta_1, D\widehat{\mathbb{J}}(q)[\widehat{\mathbb{J}}(q)\eta_2]\eta_3 \rangle + \langle \eta_2, D\widehat{\mathbb{J}}(q)[\widehat{\mathbb{J}}(q)\eta_3]\eta_1 \rangle + \langle \eta_3, D\widehat{\mathbb{J}}(q)[\widehat{\mathbb{J}}(q)\eta_1]\eta_2 \rangle = 0. \quad (15)$$

The central conditions connecting $\widehat{\mathbb{J}}$, $\widehat{\mathbb{K}}$, \mathcal{E} , and \mathcal{S} ask that the energy functional does not contribute to dissipative mechanisms and that the entropy functional does not contribute to reversible dynamics, which is encoded in the following *non-interaction conditions*:

$$(\text{NIC}) \quad \forall q \in \mathcal{Q}: \quad \widehat{\mathbb{J}}(q)D\mathcal{S}(q) = 0 \quad \text{and} \quad \widehat{\mathbb{K}}(q)D\mathcal{E}(q) = 0. \quad (16)$$

In summary, the quintuple $(\mathcal{Q}, \mathcal{E}, \mathcal{S}, \widehat{\mathbb{J}}, \widehat{\mathbb{K}})$ is called a GENERIC system, if the conditions (13)–(16) hold.

Of course, the structure of GENERIC is geometric in the sense that it is invariant under coordinate transformations, see [22]. The first observation is that (14) and (16) imply energy conservation and entropy increase:

$$\frac{d}{dt}\mathcal{E}(q(t)) = \langle D\mathcal{E}(q), \dot{q} \rangle = \langle D\mathcal{E}(q), \widehat{\mathbb{J}}(q)D\mathcal{E}(q) + \widehat{\mathbb{K}}(q)D\mathcal{S}(q) \rangle = 0 + 0 = 0, \quad (17)$$

$$\frac{d}{dt}\mathcal{S}(q(t)) = \langle D\mathcal{S}(q), \dot{q} \rangle = \langle D\mathcal{S}(q), \widehat{\mathbb{J}}(q)D\mathcal{E}(q) + \widehat{\mathbb{K}}(q)D\mathcal{S}(q) \rangle = 0 + \langle D\mathcal{S}, \widehat{\mathbb{K}}D\mathcal{S} \rangle \geq 0. \quad (18)$$

Of course, to guarantee energy conservation and positivity of the entropy production one needs much less than the two conditions (14) and (16).

However, the *maximum entropy principle* really relies on (16). It states that a maximizer q_* of \mathcal{S} subject to the constraint $\mathcal{E}(q) = E_0$ is an equilibrium of (12), the so-called thermodynamic equilibrium for the given energy. Indeed, if q_* maximizes \mathcal{S} under the constraint $\mathcal{E}(q) = E_0$, then we obtain a Lagrange multiplier $\lambda_* \in \mathbb{R}$ such that $D\mathcal{S}(q_*) = \lambda_* D\mathcal{E}(q_*)$. Since $D\mathcal{S}(q) \neq 0$ for all q (e.g., by $\partial_\theta \mathcal{S} > 0$), we have $\lambda_* \neq 0$ and conclude $\widehat{\mathbb{J}}(q_*)D\mathcal{E}(q_*) = \frac{1}{\lambda_*}\widehat{\mathbb{J}}(q_*)D\mathcal{S}(q_*) = 0$ and

$\widehat{\mathbb{K}}(q_*)\mathcal{D}\mathcal{S}(q_*) = \lambda_*\widehat{\mathbb{K}}(q_*)\mathcal{D}\mathcal{E}(q_*) = 0$, where we have used the non-interaction condition (16). Vice versa, every steady state q_* of (12) satisfies

$$\widehat{\mathbb{J}}(q_*)\mathcal{D}\mathcal{E}(q_*) = 0 \quad \text{and} \quad \widehat{\mathbb{K}}(q_*)\mathcal{D}\mathcal{S}(q_*) = 0. \quad (19)$$

Thus, in a steady state there cannot be any balancing between reversible and irreversible forces, both have to vanish independently.

The Onsager operator $\widehat{\mathbb{K}}(q)$ defines the linear kinetic relation between the entropic driving force $\eta = \mathcal{D}\mathcal{S}(q)$ and the dissipative flux $\dot{q}^{\text{diss}} = \widehat{\mathbb{K}}(q)\eta$. In many applications one needs to consider nonlinear kinetic relations $\dot{q}^{\text{diss}} \leftrightarrow \eta$. For this we use so-called dual dissipation potentials $\mathcal{R}^*(q, \cdot) : T_q^*\mathcal{Q} \rightarrow [0, \infty]$, which are lower semicontinuous, convex, and satisfy $\mathcal{R}^*(q, 0) = 0$. Then, the kinetic relation is given in the form

$$\dot{q}^{\text{diss}} = \mathcal{D}_\eta \mathcal{R}^*(q, \eta),$$

see [9, 8, 22, 17]. The linear Onsager case is included via quadratic dual dissipation potentials $\mathcal{R}^*(q, \eta) = \frac{1}{2}\langle \eta, \widehat{\mathbb{K}}(q)\eta \rangle$. The generalized version of the second non-interaction condition in (16) then reads $\mathcal{R}^*(q, \lambda\mathcal{D}\mathcal{E}(q)) = 0$ for all $\lambda \in \mathbb{R}$.

In many situations the evolution equations satisfy additional conservation laws, such as mass or charge balance. If $C : \mathcal{Q} \rightarrow \mathbb{R}$ is a such a conserved quantity, then the GENERIC system should also satisfy both $\langle \mathcal{D}C(q), \widehat{\mathbb{J}}(q)\mathcal{D}\mathcal{E}(q) \rangle = 0$ and $\langle \mathcal{D}C(q), \widehat{\mathbb{K}}(q)\mathcal{D}\mathcal{S}(q) \rangle = 0$ for all $q \in \mathcal{Q}$.

3.2 Damped Hamiltonian systems

If temperature effects are negligible, GENERIC systems can be simplified by assuming constant temperature θ and using the free energy $\mathcal{F}(q) := \mathcal{E}(q) - \theta\mathcal{S}(q)$. We call a quadruple $(\mathcal{Q}, \mathcal{F}, \mathbb{J}, \mathbb{K})$ a *damped Hamiltonian system*, if \mathcal{F} is a sufficiently smooth functional on \mathcal{Q} and if \mathbb{J} and \mathbb{K} satisfy (13) and (14), but no non-interaction condition is needed. If we have a linear Onsager operator \mathbb{K} or a more general dual dissipation potential $\widehat{\mathcal{R}}^*$, the associated evolution equations read

$$\dot{q} = (\mathbb{J}(q) - \mathbb{K}(q))\mathcal{D}\mathcal{F}(q) \quad \text{or} \quad \dot{q} = \mathbb{J}(q)\mathcal{D}\mathcal{F}(q) + \mathcal{D}_\eta \mathcal{R}^*(q, -\mathcal{D}\mathcal{F}(q)), \quad (20)$$

respectively. Of course, we still may have conserved quantities $C : \mathcal{Q} \rightarrow \mathbb{R}$; then we always ask to have $\langle \mathcal{D}C(q), \mathbb{J}(q)\mathcal{D}\mathcal{F}(q) \rangle = 0 = \langle \mathcal{D}C(q), \mathbb{K}(q)\mathcal{D}\mathcal{F}(q) \rangle$ for all $q \in \mathcal{Q}$.

Every damped Hamiltonian system can be augmented to become a GENERIC system with constant temperature $\theta > 0$ as follows. We introduce a scalar entropy variable $s \in \mathbb{R}$ and set

$$y = (q, s), \quad Y = \mathcal{Q} \times \mathbb{R}, \quad \mathcal{E}(q, s) = \mathcal{F}(q) + \theta s, \quad \mathcal{S}(q, s) = s, \\ \widehat{\mathbb{J}}(q, s) = \begin{pmatrix} \mathbb{J}(q) & 0 \\ 0 & 0 \end{pmatrix}, \quad \widehat{\mathbb{K}}(q, s) = \begin{pmatrix} \mathbb{K}(q) & -\mathbb{K}(q)\mathcal{D}\mathcal{F}(q) \\ -\langle \square, \mathbb{K}(q)\mathcal{D}\mathcal{F}(q) \rangle & \frac{1}{\theta}\langle \mathcal{D}\mathcal{F}(q), \mathbb{K}(q)\mathcal{D}\mathcal{F}(q) \rangle \end{pmatrix}.$$

Then $(Y, \mathcal{E}, \mathcal{S}, \widehat{\mathbb{J}}, \widehat{\mathbb{K}})$ is a GENERIC system generating the evolution (20) for q and the entropy balance $\dot{s} = \frac{1}{\theta}\langle \mathcal{D}\mathcal{F}(q), \widehat{\mathbb{K}}(q)\mathcal{D}\mathcal{F}(q) \rangle$, which immediately gives $\dot{s} \geq 0$.

3.3 Additive structure of dissipative contributions

As observed in [24, Sec. 2.2] the representation of the dissipative parts of the dynamics in terms of Onsager operators or dual dissipation potentials has the major advantage that there is often

an additive structure. Indeed, given \mathcal{E} the set of operators \mathbb{K} satisfying (13), (14), and (16) is a convex cone, i.e., if \mathbb{K}_1 and \mathbb{K}_2 satisfy the conditions, then $\alpha_1 \mathbb{K}_1 + \alpha_2 \mathbb{K}_2$ does so as well for all $\alpha_1, \alpha_2 \geq 0$. A similar statement is not true for the Poisson structures \mathbb{J} , because Jacobi's identity (15) is nonlinear.

The additive structure will be useful in modeling complex semiconductor devices, since we are able to consider different dissipative processes as independent building blocks each giving rise to one \mathbb{K}_j and then simply add these operators, or similarly for dual dissipation potentials. Thus, we will use the form

$$\mathbb{K} = \mathbb{K}_{\text{diffusion}} + \mathbb{K}_{\text{reaction}} + \mathbb{K}_{\text{quant-class}} + \mathbb{K}_{\text{heat.cond.}} + \mathbb{K}_{\text{bulk-interface}}.$$

In the present work we will ignore temperature effects and bulk-interface interactions and refer to [22, 23, 24] for the modeling of heat transfer via $\mathbb{K}_{\text{heat.cond.}}$ and to [7, 17] for bulk-interface interactions encoded in $\mathbb{K}_{\text{bulk-interface}}$.

3.4 Dissipative coupling between different components

The construction of couplings between different components of a system, such as classical charge carriers and the state of a quantum system, can be done efficiently in terms of Onsager operators, thus building the Onsager symmetry into the system automatically. Assume that \mathcal{Q} is given in the form $q = (q_1, q_2) \in \mathcal{Q}_1 \times \mathcal{Q}_2 = \mathcal{Q}$ and denote by $\eta_1 \in \mathcal{Q}_1^*$ and $\eta_2 \in \mathcal{Q}_2^*$ the corresponding conjugate thermodynamical driving forces.

As we want to couple η_1 and η_2 we introduce a third linear space \mathbf{X} (which may also be \mathcal{Q}_1^* or \mathcal{Q}_2^*) and linear mappings $A_j(q) : \mathcal{Q}_j^* \rightarrow \mathbf{X}$ and an Onsager operator $\mathbb{K}_{\mathbf{X}}(q) : \mathbf{X}^* \rightarrow \mathbf{X}$ to define a dual dissipation potential

$$\mathcal{R}_{\text{coupl}}^*(q; \eta_1, \eta_2) := \frac{1}{2} \langle A_1(q)\eta_1 + A_2(q)\eta_2, \mathbb{K}_{\mathbf{X}}(q)(A_1(q)\eta_1 + A_2(q)\eta_2) \rangle_{\mathbf{X}}.$$

For a GENERIC system we additionally ask for the non-interaction condition $\mathcal{R}^*(q, \lambda D\mathcal{E}(q)) = 0$.

The dual dissipation potential $\mathcal{R}_{\text{coupl}}^*$ defines the Onsager operator $\mathbb{K}_{\text{coupl}}(q) : \mathcal{Q}^* \rightarrow \mathcal{Q}$, which takes the following block structure with respect to the decomposition $\mathcal{Q} = \mathcal{Q}_1 \times \mathcal{Q}_2$:

$$\mathbb{K}_{\text{coupl}}(q) = \begin{pmatrix} A_1^*(q)\mathbb{K}_{\mathbf{X}}(q)A_1(q) & A_1^*(q)\mathbb{K}_{\mathbf{X}}(q)A_2(q) \\ A_2^*(q)\mathbb{K}_{\mathbf{X}}(q)A_1(q) & A_2^*(q)\mathbb{K}_{\mathbf{X}}(q)A_2(q) \end{pmatrix}.$$

In addition to quantum-classical coupling this method can also be used to couple the interaction between bulk effects and interfacial effects, where A_j may be a trace operator, see [7].

4 Semiconductor modeling via damped Hamiltonian systems

We now show how the above concepts of damped Hamiltonian systems can be used to construct thermodynamically consistent models for semiconductor devices including arbitrarily many charge carriers $\mathbf{c} = (c_1, \dots, c_{i_*})$, where the number of species is denoted by i_* , as well as a quantum system described by a finite-dimensional density matrix ρ .

First, we recover the van Roosbroeck system for the carrier densities $\mathbf{c} = (n, p)$ considered in Section 2 to highlight the simplicity of the gradient structure constructed in [23]. Then, we show

how this structure generalizes to arbitrarily many species and to general statistics. Next, we review recent results on the gradient structure for the dissipative part of open quantum systems described by the Lindblad master equation [29]. Finally, we show how the coupling strategy developed in Section 3.4 can be adapted to model the interaction of macroscopic thermodynamical systems and open quantum systems.

4.1 The state variables and free energy

Throughout we consider a domain $\Omega \subset \mathbb{R}^d$ in which all the charge carriers move and interact. The carrier densities are denoted by $c_i(t, x)$ with $t \in [0, T]$, $x \in \Omega$ and $i \in \{1, \dots, i_*\}$. Moreover, we assume that there is a population of identical quantum dots each of which is described by a density matrix

$$\rho \in \mathfrak{R}_n := \{ \rho \in \mathbb{C}^{n \times n} \mid \rho = \rho^*, \rho \geq 0, \text{tr } \rho = 1 \}.$$

We assume that the distance between the quantum dots is sufficiently big, such that they do not interact directly. However, we assume that there are still enough quantum dots such that we can model the states by a continuum description via a function $\rho(t, x) \in \mathfrak{R}_n$.

In total our state space \mathcal{Q} for $q = (\rho, \mathbf{c})$ will be given as

$$\mathcal{Q} = \mathcal{Q}_{\text{quant}} \times \mathcal{Q}_{\text{carr}} \quad \text{with } \mathcal{Q}_{\text{quant}} := L^1(\Omega; \mathfrak{R}_n) \text{ and } \mathcal{Q}_{\text{carr}} := L^1(\Omega; [0, \infty)^{i_*}).$$

Of course, from the modeling perspective there are many other options to “localize” the charge carriers of the quantum system, e.g., by constructing models with several dimensions. In the case of wetting layers, certain charge carrier species may live only on a submanifold, see e.g. [7]. A single quantum dot embedded into a bulk material can be considered by means of a weight function as it was done in [14]. Such situations can also be modeled by the approach presented here, but for notational simplicity we stick with the setup as given above.

On the state space $\mathcal{Q} = \mathcal{Q}_{\text{quant}} \times \mathcal{Q}_{\text{carr}}$ we consider the free energy functional

$$\mathcal{F}(\rho, \mathbf{c}) = \int_{\Omega} \left(\frac{\varepsilon}{2} |\nabla \Phi_{\rho, \mathbf{c}}|^2 + \rho_{\text{qd}} \text{tr}(\rho \mathbf{H} + E_{\beta} \rho \log \rho) + F_{\text{carr}}(\mathbf{c}) \right) dx, \quad (21)$$

where $E_{\beta} = k_B \theta = \beta^{-1}$ is the inverse thermal energy, ρ_{qd} is the volume density of quantum dots, \mathbf{H} is the Hamiltonian of the quantum system and $F_{\text{carr}}(\mathbf{c})$ is the free energy density of the classical carrier system. The electrostatic potential $\Phi_{\rho, \mathbf{c}} = \phi_{\rho, \mathbf{c}} - \phi_{\text{eq}}$ is defined in terms of the Poisson problem

$$-\text{div}(\varepsilon \nabla \phi_{\rho, \mathbf{c}}) = e_0 (C + \mathbf{z} \cdot \mathbf{c} + \rho_{\text{qd}} \text{tr}(\mathbf{Z} \rho)) \quad \text{on } \Omega, \quad \mathbf{v} \cdot \nabla \phi_{\rho, \mathbf{c}} = 0 \quad \text{on } \partial \Omega. \quad (22)$$

Here $\mathbf{z} = (z_1, \dots, z_{i_*}) \in \mathbb{Z}^{i_*}$ is the vector of charge numbers associated with \mathbf{c} , while $\mathbf{Z} \in \mathbb{C}^{n \times n}_{\text{herm}}$ is the charge number operator for the quantum system. The vector \mathbf{c}_{eq} of equilibrium carrier densities and the equilibrium density matrix ρ_{eq} define the equilibrium electrostatic potential $\phi_{\text{eq}} := \phi_{\rho_{\text{eq}}, \mathbf{c}_{\text{eq}}}$, such that under equilibrium conditions we have $\Phi_{\rho, \mathbf{c}} \equiv 0$. For the sake of simplicity, we restrict ourselves to a closed system with homogeneous Neumann boundary conditions (11).

4.2 The van Roosbroeck system as gradient system

The free energy density associated with the van Roosbroeck system (3) for the density of electrons and holes $\mathbf{c} = (n, p)$ consists of the sum of the relative entropies for the two species and

the electrostatic energy

$$\mathcal{F}_{\text{vR}}(n, p) = \int_{\Omega} \left(\frac{\varepsilon}{2} |\nabla \Phi_{n,p}|^2 + E_{\beta} \lambda_{\text{B}}(n/n_{\text{eq}}) n_{\text{eq}} + E_{\beta} \lambda_{\text{B}}(p/p_{\text{eq}}) p_{\text{eq}} \right) dx$$

with $\lambda_{\text{B}}(z) := z \log z - z + 1$. The electrostatic potential $\Phi_{n,p}$ solves the Poisson problem (22) without the quantum mechanical part. Here we restrict our considerations to non-degenerate carrier ensembles (Maxwell–Boltzmann statistics) with $F_{\text{carr}}(\mathbf{c}) = F_{\text{B}}(n, p)$. For the structure of the free energy functional in the case of Fermi–Dirac statistics we refer to [1].

When taking the variational derivatives of \mathcal{F}_{vR} with respect to n and p we have to take into account the linear dependence of $\Phi_{n,p}$ on n and p given in terms of (22). Then we find

$$\boldsymbol{\mu} = \begin{pmatrix} \mu_n \\ \mu_p \end{pmatrix} = D\mathcal{F}_{\text{vR}}(n, p) = \begin{pmatrix} E_{\beta} \log(n/n_{\text{eq}}) - e_0 \Phi_{n,p} \\ E_{\beta} \log(p/p_{\text{eq}}) + e_0 \Phi_{n,p} \end{pmatrix}, \quad (23)$$

where μ_n and μ_p are the electro-chemical potentials that are thermodynamically conjugate to n and p , respectively (see Section 2.1). The different signs in front of $e_0 \Phi_{n,p}$ reflect the charges of electrons and holes and arise because of the different signs in front of n and p in (22).

The gradient structure for the van Roosbroeck system developed in [23] is completed by the Onsager operator

$$\mathbb{K}_{\text{vR}}(n, p) \begin{pmatrix} \mu_n \\ \mu_p \end{pmatrix} = - \begin{pmatrix} \operatorname{div}(\frac{1}{e_0} \mathbb{M}_n n \nabla \mu_n) \\ \operatorname{div}(\frac{1}{e_0} \mathbb{M}_p p \nabla \mu_p) \end{pmatrix} + \frac{r(n, p)}{k_{\text{B}} \theta} \Lambda(np, n_{\text{eq}} p_{\text{eq}}) \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} \mu_n \\ \mu_p \end{pmatrix}, \quad (24)$$

where $\Lambda(a, b) = \int_0^1 a^s b^{1-s} ds = (a - b)/\log(a/b)$ is the logarithmic mean of a and b . Note that \mathbb{K}_{vR} is the sum of a transport part, which gives rise to drift and diffusion, and a reaction part.

Using the identities $c \nabla(\log c) = \nabla c$ and $\Lambda(a, b)(\log a - \log b) = a - b$, it is easy to see that the equations of motion generated by (23) and (24) read

$$\begin{pmatrix} \dot{n} \\ \dot{p} \end{pmatrix} = -\mathbb{K}_{\text{vR}}(n, p) D\mathcal{F}_{\text{vR}}(n, p) = - \begin{pmatrix} \operatorname{div} \mathbf{J}_n + R(n, p) \\ \operatorname{div} \mathbf{J}_p + R(n, p) \end{pmatrix},$$

which are the continuity equations (3b)–(3c). Here we have used (7) and (9). Hence, the van Roosbroeck system has indeed a gradient flow structure that is generated by a gradient system $(\mathcal{Q}_{\text{vR}}, \mathcal{F}_{\text{vR}}, \mathbb{K}_{\text{vR}})$ with $\mathcal{Q}_{\text{vR}} = \{(n, p) \in L^1(\Omega)^2 \mid p, n \geq 0 \text{ a.e.}\}$. The total charge $C(n, p) = \int_{\Omega} (n - p) dx$ is a conserved quantity.

In the following subsection we will show how this can be generalized to an arbitrary number of charge carrier densities c_i , $i = 1, \dots, i_*$. Based on the fundamental work [1] it is shown in [23, Sec. 4.2] how temperature effects can be taken into account by using the physical entropy as a driving functional.

4.3 Reactions between and transport of charge carriers

The charge carriers $\mathbf{c} = (n, p)$ can react in various ways, in particular they can be annihilated in recombination processes. The generation of electron-hole pairs is written as $\emptyset \rightarrow X_n + X_p$ and the recombination of electron-hole pairs reads $X_n + X_p \rightarrow \emptyset$. In the limit of small carrier densities, the reaction rate equation is of so-called *mass-action type* and reads

$$\dot{n}|_{\text{react}} = - \left(k^{\text{fw}} np - k^{\text{bw}} \right), \quad \dot{p}|_{\text{react}} = - \left(k^{\text{fw}} np - k^{\text{bw}} \right).$$

The forward and backward coefficients k^{fw} and k^{bw} may depend on the variables of the system giving $r(n, p) = k^{\text{fw}}$ and $n_{\text{eq}} p_{\text{eq}} = k^{\text{bw}} / k^{\text{fw}}$ in (9). Moreover, they involve several material-dependent parameters. An important feature is the conservation of charge, namely $(\dot{p} - \dot{n})|_{\text{react}} \equiv 0$.

More general, we consider m_* reactions of mass-action type for the charge carrier species X_1, X_2, \dots, X_{i_*} . They are defined in terms of the forward and backward stoichiometric coefficients α_i^m and β_i^m , respectively, via

$$\alpha_1^m X_1 + \dots + \alpha_{i_*}^m X_{i_*} \rightleftharpoons \beta_1^m X_1 + \dots + \beta_{i_*}^m X_{i_*}.$$

With $\mathbf{c}^\gamma := \prod_{i=1}^{i_*} c_i^{\gamma_i}$ this leads to the reaction-rate equation

$$\dot{\mathbf{c}}|_{\text{react}} = -\mathbf{R}(\mathbf{c}) := -\sum_{m=1}^{m_*} (k_m^{\text{fw}} \mathbf{c}^{\alpha^m} - k_m^{\text{bw}} \mathbf{c}^{\beta^m}) (\alpha^m - \beta^m), \quad (25)$$

where the stoichiometric vectors α^m and β^m lie in $\mathbb{N}_0^{i_*}$ and satisfy the condition of electro-neutrality $(\alpha^m - \beta^m) \cdot \mathbf{z} \equiv 0$.

The condition of detailed balance means that there exists a positive density vector $\mathbf{c}_{\text{eq}} \in]0, \infty[^{i_*}$ such that all reactions are in equilibrium, i.e., $\bar{k}_m = k_m^{\text{fw}} \mathbf{c}_{\text{eq}}^{\alpha^m} = k_m^{\text{bw}} \mathbf{c}_{\text{eq}}^{\beta^m}$. It was observed in [45, 23] that (25) with its polynomial right-hand side is generated by the gradient system $(]0, \infty[^{i_*}, F_B, \mathbb{K}_{\text{react}})$ if the m_* reactions satisfy this detailed balance condition: Setting $F_{\text{carr}}(\mathbf{c}) = F_B(\mathbf{c}) := k_B \theta \sum_{i=1}^{i_*} \lambda_B(c_i / c_i^{\text{eq}}) c_i^{\text{eq}}$ with $\lambda_B(z) = z \log z - z + 1$, we obtain

$$\begin{aligned} \dot{\mathbf{c}}|_{\text{react}} &= -\mathbf{R}(\mathbf{c}) = -\mathbb{K}_{\text{react}}(\mathbf{c}) D F_B(\mathbf{c}) \\ \text{and } \mathbb{K}_{\text{react}}(\mathbf{c}) &= \frac{1}{k_B \theta} \sum_{m=1}^{m_*} \bar{k}_m \Lambda(\widehat{\mathbf{c}}^{\alpha^m}, \widehat{\mathbf{c}}^{\beta^m}) (\alpha^m - \beta^m) \otimes (\alpha^m - \beta^m) \geq 0. \end{aligned} \quad (26)$$

Here $\widehat{\mathbf{c}} := (c_i / c_i^{\text{eq}})_{i=1, \dots, i_*}$ is the vector of relative densities, and $\Lambda(a, b)$ is the logarithmic mean. We emphasize that $\mathbb{K}_{\text{react}}$ is a sum over the individual contribution of each of the m_* reactions. Of course, the coefficients \bar{k}_m may depend on the whole state \mathbf{c} without destroying the gradient structure.

Because of charge neutrality it doesn't matter whether we use the chemical potentials $\boldsymbol{\eta} = D F_B(\mathbf{c})$ or the electro-chemical potentials $\boldsymbol{\mu} = D \mathcal{F}(\mathbf{c}) = \boldsymbol{\eta} + e_0 \Phi_{\mathbf{c}} \mathbf{z}$ as driving forces. Moreover, the total charge $C(\mathbf{c}) := \int_{\Omega} \mathbf{z} \cdot \mathbf{c}(x) dx$ is a conserved quantity.

Remark 1 In [27] a gradient structure for reaction-rate equations was derived via a large-deviation principle for the underlying chemical master equation. It leads to the same free energy F_B but to a non-quadratic dual dissipation potential, namely

$$\begin{aligned} \mathcal{R}^*(\mathbf{c}, \boldsymbol{\mu}) &= \sum_{m=1}^{m_*} \frac{\bar{k}_m}{k_B \theta} (\widehat{\mathbf{c}}^{\alpha^m} \widehat{\mathbf{c}}^{\beta^m})^{1/2} C_*((\alpha^m - \beta^m) \cdot \boldsymbol{\mu}) \\ \text{with } C_*(\xi) &= 4 \cosh\left(\frac{\xi}{2}\right) - 4. \end{aligned} \quad (27)$$

See also [8, Eqn. (69)] for the occurrence of the cosh potential in chemical reactions.

4.4 Gradient structure for general carrier statistics

We emphasize that the structure of (26) looks very special and is chosen in order to produce a simple polynomial right-hand side \mathbf{R} in the case of Maxwell–Boltzmann statistics. However, the

gradient structure is still valid for more general statistics. Indeed we may consider a free energy density $F_{\text{carr}}(\mathbf{c})$ for the charge carriers that involves more general statistical distribution functions (e.g., Fermi–Dirac statistics) and then choose $\mathbb{K}_{\text{react}}(\mathbf{c}) = \sum_{m=1}^{m_*} \kappa_m(\mathbf{c})(\boldsymbol{\alpha}^m - \boldsymbol{\beta}^m) \otimes (\boldsymbol{\alpha}^m - \boldsymbol{\beta}^m)$ with suitable scalar coefficients $\kappa_m(\mathbf{c})$. In this way one keeps the gradient structure and hence the thermodynamic principles even without the mass-action type kinetics.

The transport of charge carriers occurs by diffusion as well as by drift in the electric field $\mathbf{E} = -\nabla\Phi_{\mathbf{c}}$. The thermodynamical driving force is the electro-chemical potential

$$\boldsymbol{\mu} = D\mathcal{F}(\mathbf{c}) = \boldsymbol{\eta} + e_0\Phi_{\mathbf{c}}\mathbf{z} \quad \text{with} \quad \boldsymbol{\eta} = DF_{\text{carr}}(\mathbf{c}),$$

that can be split into the chemical potentials $\boldsymbol{\eta} = DF_{\text{carr}}(\mathbf{c})$ and the electrostatic forces involving the charge numbers z_i of the respective carrier species. The associated fluxes $\mathbf{J}_i \in \mathbb{R}^d$ can be combined into a matrix $\mathbf{J}_{\mathbf{c}} \in \mathbb{R}^{i_* \times d}$. Within the framework of linear irreversible thermodynamics [31], the classical ansatz is

$$\mathbf{J}_{\mathbf{c}} = -\mathbf{M}(\mathbf{c})\nabla\boldsymbol{\mu} = -\mathbf{M}(\mathbf{c})(\nabla\boldsymbol{\eta} + \mathbf{z} \otimes \nabla\Phi_{\mathbf{c}}), \quad (28)$$

where the conductivity tensor \mathbf{M} is symmetric and positive semi-definite mapping $\mathbb{R}^{i_* \times d}$ into itself. In the isotropic case one may choose $\mathbf{M}(\mathbf{c}) \in \mathbb{R}^{i_* \times i_*}$, e.g., $\mathbf{M}(\mathbf{c}) = \text{diag}(m_i c_i)_{i=1, \dots, i_*}$.

The Onsager operator $\mathbb{K}_{\text{transp}}$ for transport of charge carriers is now given in the form

$$\mathbb{K}_{\text{transp}}(\mathbf{c})\boldsymbol{\mu} = -\text{div}(\mathbf{M}(\mathbf{c})\nabla\boldsymbol{\mu}).$$

Thus, for general situations the reactions and transport for the carrier density vector \mathbf{c} can be written as a gradient system in the form

$$\begin{aligned} \dot{\mathbf{c}} &= -(\mathbb{K}_{\text{transp}}(\mathbf{c}) + \mathbb{K}_{\text{react}}(\mathbf{c}))D\mathcal{F}(\mathbf{c}) \\ &= \text{div}(\mathbf{M}(\mathbf{c})(\nabla DF_{\text{carr}}(\mathbf{c}) + \mathbf{z} \otimes \nabla\Phi_{\mathbf{c}})) - \mathbb{K}_{\text{react}}(\mathbf{c})DF_{\text{carr}}(\mathbf{c}), \end{aligned}$$

where we used electro-neutrality of the reactions, i.e., $\mathbb{K}_{\text{react}}(\mathbf{c})\mathbf{z} \equiv 0$. In the case of nontrivial carrier statistics $F_{\text{carr}} \neq F_{\text{B}}$ the Hessian of the carrier's free energy density $\nabla DF_{\text{carr}}(\mathbf{c}) = D^2 F_{\text{carr}}(\mathbf{c})\nabla\mathbf{c} \in \mathbb{R}^{i_* \times d}$ gives rise to nonlinear diffusion [21, 15].

4.5 Dissipative quantum mechanics

Here we show how dissipative quantum systems subject to the Lindblad master equation can be written as a damped Hamiltonian system with respect to the von Neumann entropy, if the dissipative part satisfies a suitable detailed balance condition.

A Markovian quantum master equation (see, e.g., [19, 41, 43, 4]) in Lindblad form reads

$$\dot{\boldsymbol{\rho}} = \mathcal{J}[\boldsymbol{\rho}, H] + \mathfrak{D}\boldsymbol{\rho}, \quad \text{where} \quad \mathfrak{D}\boldsymbol{\rho} = \sum_{k=1}^{k_*} \alpha_k \mathbb{G}_Q \boldsymbol{\rho} \quad (29)$$

with

$$\mathbb{G}_Q A := \frac{1}{2} ([Q, A Q^*] + [Q A, Q^*]). \quad (30)$$

The coupling operators $Q \in \mathbb{C}^{n \times n}$ and the transition rates $\alpha_k \in [0, \infty[$ are arbitrary and \mathfrak{D} is called the dissipation superoperator. We use the notation $j = i/\hbar$.

With the derivative $D\mathcal{F}_{\text{quant}}(\boldsymbol{\rho}) = H + E_\beta \log \boldsymbol{\rho}$ (up to a constant) of the free energy functional $\mathcal{F}_{\text{quant}}(\boldsymbol{\rho}) = \text{tr}(H\boldsymbol{\rho} + E_\beta \boldsymbol{\rho} \log \boldsymbol{\rho})$, the Hamiltonian part has the desired form

$$J[\boldsymbol{\rho}, H] = J[\boldsymbol{\rho}, D\mathcal{F}_{\text{quant}}(\boldsymbol{\rho})] = \mathbb{J}_{\text{quant}}(\boldsymbol{\rho}) D\mathcal{F}_{\text{quant}}(\boldsymbol{\rho}) \quad \text{with } \mathbb{J}_{\text{quant}}(\boldsymbol{\rho}) A := J[\boldsymbol{\rho}, A].$$

The Jacobi identity (15) for $\mathbb{J}_{\text{quant}}$ follows from the elementary Jacobi identity for the commutator.

Thus it remains to write $\mathfrak{D}\boldsymbol{\rho}$ in the form $-\mathbb{K}(\boldsymbol{\rho}) D\mathcal{F}_{\text{quant}}(\boldsymbol{\rho})$. This problem was first solved in [5, 29], again relying on a suitable non-commutative version of a detailed balance condition. In Section 4.7 we will show how the coefficients α_k may be chosen to depend on \boldsymbol{c} , if there are corresponding back-coupling terms in the reaction equation. For this we exploit the coupling technique introduced in Section 3.4.

The main structure is a non-commutative version of the chain-rule identities $c \nabla \log c = \nabla c$ for diffusion (cf. Section 4.2) and $\Lambda(c_i^\alpha, c_j^\beta)(\alpha \log c_i - \beta \log c_j) = c_i^\alpha - c_j^\beta$ for reactions of mass-action type (cf. Section 4.3). As highlighted in [33, 34], the proper generalization is obtained via the Kubo–Mori multiplication operator

$$\mathfrak{C}_\rho : A \mapsto \int_0^1 \rho^s A \rho^{1-s} ds.$$

Kubo’s miracle identity (see [16, 44]) then states that

$$\forall Q \in \mathbb{C}^{n \times n} \forall \rho \in \mathfrak{R}_n : \quad \mathfrak{C}_\rho[Q, \log \rho] = [Q, \rho].$$

The above formula is not sufficient to treat terms of the form $[Q, \log \rho + \beta H]$. However, when restricting to a suitable subclass of operators Q , a generalized miracle identity can be obtained. For this we choose eigenpairs (ω, Q) of the commutator operator $A \mapsto [A, H]$, viz.

$$[Q, H] = \hbar \omega Q. \tag{31}$$

Using two eigenstates ψ_1 and ψ_2 with $H\psi_j = h_j\psi_j$ with energy levels $h_j \in \mathbb{R}$, we see that $Q = \psi_1 \otimes \psi_2$ satisfies (31) with $\hbar \omega = h_2 - h_1$. The following generalization of the miracle identity relies on doubling the dimension by considering

$$\mathbb{B}_Q := \begin{pmatrix} 0 & Q^* \\ Q & 0 \end{pmatrix} \in \mathbb{C}_{\text{Herm}}^{2n \times 2n} \quad \text{and} \quad \mathbb{R}(\rho, \gamma) := \begin{pmatrix} e^{\gamma/2} \rho & 0 \\ 0 & e^{-\gamma/2} \rho \end{pmatrix} \in \mathbb{C}_{\text{Herm}}^{2n \times 2n}.$$

Using (ω, Q) satisfying (31) and the doubling operator $\mathbb{X} : \mathbb{C}^{n \times n} \rightarrow \mathbb{C}^{2n \times 2n}; A \mapsto \begin{pmatrix} A & 0 \\ 0 & A \end{pmatrix}$ we obtain the *generalized miracle identity*

$$\begin{aligned} \mathfrak{C}_{\mathbb{R}(\rho, \beta \hbar \omega)} [\mathbb{B}_Q, \mathbb{X}(H + E_\beta \log \rho)] &= [\mathbb{B}_Q, \mathbb{R}(\rho, \beta \hbar \omega)] \\ &= \begin{pmatrix} 0 & e^{-\beta \hbar \omega/2} Q^* \rho - e^{\beta \hbar \omega/2} \rho Q^* \\ e^{\beta \hbar \omega/2} Q \rho - e^{-\beta \hbar \omega/2} \rho Q & 0 \end{pmatrix}, \end{aligned} \tag{32}$$

where again the right-hand side is linear in ρ . As shown in [29], see also [5] for related results, this identity follows simply from the miracle identity applied to $\mathbb{R}(\rho, \gamma)$ and \mathbb{B}_Q and the fact that (31) implies the commutator result

$$[\mathbb{B}_Q, \log \mathbb{R}(\rho, \beta \hbar \omega)] = \left[\mathbb{B}_Q, \begin{pmatrix} \frac{1}{2} \beta \hbar \omega I + \log \rho & 0 \\ 0 & -\frac{1}{2} \beta \hbar \omega I + \log \rho \end{pmatrix} \right] = \beta [\mathbb{B}_Q, \mathbb{X}(H + E_\beta \log \rho)].$$

This construction allows us to define dual dissipation potentials, where we can take a sum over a set (ω_k, Q_k) of eigenpairs satisfying (31), namely

$$\mathcal{R}_{\text{quant}}^*(\rho, \sigma) = \beta \sum_{k=1}^{k_*} \frac{\alpha_k}{2} \text{tr} \left(([\mathbb{B}_{Q_k}, \mathbb{X}\sigma])^* \mathfrak{C}_{R(\rho, \beta \hbar \omega_k)} [\mathbb{B}_{Q_k}, \mathbb{X}\sigma] \right),$$

where $\alpha_k \geq 0$. Because the adjoint \mathbb{X}^* satisfies $\mathbb{X}^* \begin{pmatrix} A & B \\ C & D \end{pmatrix} = A + D$ we obtain the associated Onsager operator, which depends highly nontrivial on ρ :

$$\mathbb{K}_{\text{quant}}(\rho) \sigma = -\beta \sum_{k=1}^{k_*} \alpha_k \mathbb{X}^* \left[\mathbb{B}_{Q_k}, \mathfrak{C}_{R(\rho, \beta \hbar \omega_k)} [\mathbb{B}_{Q_k}, \mathbb{X}\sigma] \right]. \quad (33)$$

Exploiting the generalized miracle identity (32) we find the desired Lindblad form

$$\mathbb{K}_{\text{quant}}(\rho) (H + E_\beta \log \rho) = - \sum_{k=1}^{k_*} \alpha_k (e^{\beta \hbar \omega_k / 2} \mathbb{G}_{Q_k} \rho + e^{-\beta \hbar \omega_k / 2} \mathbb{G}_{Q_k^*} \rho),$$

that features special choices for the weights of \mathbb{G}_{Q_k} and $\mathbb{G}_{Q_k^*}$ to guarantee the detailed balance condition.

4.6 The van Roosbroeck system coupled to a quantum system

Before we show how quantum mechanics can be coupled to the van Roosbroeck system via the formalism of damped Hamiltonian systems, we follow the approach in [14] and show that for simple couplings one can prove that the free energy \mathcal{F} is indeed a Liapunov function. In Section 4.7 this will follow automatically, but from very elaborate construction, while the arguments in this subsection are more intuitive and direct.

For quantum master equations of type (29) without the detailed balance condition it is much more difficult to show that the relative entropy is a Liapunov function, see [18]. In [41, 42] explicit expressions for the dissipation were derived for systems satisfying a detailed balance conditions. Exactly these formulas stimulated the gradient structure developed in the previous subsection.

To highlight the idea of consistent coupling of the van Roosbroeck system and a quantum system developed in [14], we now look at one coupling mechanism, namely the capture and escape of a free electron into a quantum dot, which can be written as a forward-backward reaction

$$X_n + \psi_1 \rightleftharpoons \psi_2,$$

where $\psi_j \in \mathbb{C}^n$ denote normalized eigenstates with $H\psi_j = h_j\psi_j$ of the Hamiltonian H . Here ψ_1 might denote a ground state (empty quantum dot) while ψ_2 denotes an excited state (electron captured by the quantum dot), see [14] for details. The eigenstates ψ_j should also satisfy $Z\psi_j = (1-j)\psi_j$ for $j = 1$ and 2 . Hence, H and Z share the same eigenbasis such that

$$[H, Z] = 0. \quad (34)$$

Physically, the condition (34) implies that the Hamiltonian evolution leaves the charge of the quantum system invariant. Therefore, the exchange of charges is necessarily a dissipative process that couples the open quantum system to the macroscopic system in its environment.

Using the transfer operator $Q = \psi_1 \otimes \psi_2 \in \mathbb{C}^{n \times n}$ and setting $\hbar\omega = h_2 - h_1$ we obtain the commutator relations

$$[Q, H] = \hbar\omega Q, \quad [Q^*, H] = -\hbar\omega Q^*, \quad [Q, Z] = -Q, \quad [Q^*, Z] = +Q^*.$$

The electron-exchange flux between the macroscopic system and the quantum dots is modeled by an additional reaction term on the right hand side of (3b)

$$R_n^{\text{quant-class}}(\boldsymbol{\rho}, n) = -\rho_{\text{qd}} \operatorname{tr}(Z \mathfrak{D}_{\text{cp}}(n) \boldsymbol{\rho}) \quad (35)$$

where the coupling operator \mathfrak{D}_{cp} is given via

$$\mathfrak{D}_{\text{cp}}(n) \boldsymbol{\rho} = \kappa(n) \left(e^{(\beta \hbar \omega + \log(n/n_{\text{eq}}))/2} \mathbb{G}_Q \boldsymbol{\rho} + e^{-(\beta \hbar \omega + \log(n/n_{\text{eq}}))/2} \mathbb{G}_{Q^*} \boldsymbol{\rho} \right) \quad (36)$$

with $\kappa \geq 0$ non-negative. The “total” dissipation superoperator in (30) is the sum $\mathfrak{D}(n) \boldsymbol{\rho} = \mathfrak{D}_0 \boldsymbol{\rho} + \mathfrak{D}_{\text{cp}}(n) \boldsymbol{\rho}$. The processes described by \mathfrak{D}_0 do not couple the open quantum system and the macroscopic system as they are assumed to not exchange carriers between both subsystems, i.e., it holds

$$\operatorname{tr}(Z \mathfrak{D}_0 \boldsymbol{\rho}) \equiv 0. \quad (37)$$

With this construction, the coupled system reads

$$0 = \operatorname{div}(\varepsilon \nabla \phi_{\boldsymbol{\rho}, n, p}) + e_0(C + p - n + \rho_{\text{qd}} \operatorname{tr}(Z \boldsymbol{\rho})), \quad (38a)$$

$$\dot{n} = -\operatorname{div} \mathbf{J}_n - R(n, p) + \rho_{\text{qd}} \operatorname{tr}(Z \mathfrak{D}_{\text{cp}}(n) \boldsymbol{\rho}), \quad (38b)$$

$$\dot{p} = -\operatorname{div} \mathbf{J}_p - R(n, p), \quad (38c)$$

$$\dot{\boldsymbol{\rho}} = \mathcal{J}[\boldsymbol{\rho}, H + e_0 \Phi_{\boldsymbol{\rho}, n, p} Z] + \mathfrak{D}_0 \boldsymbol{\rho} + \mathfrak{D}_{\text{cp}}(n) \boldsymbol{\rho}. \quad (38d)$$

As before, the electrostatic potential $\Phi_{\boldsymbol{\rho}, n, p} = \phi_{\boldsymbol{\rho}, n, p} - \phi_{\text{eq}}$ is defined via (22). The system (38) conserves the total charge, as it implies continuity equation

$$\dot{\varrho} + \operatorname{div} \mathbf{J}_{\varrho} = 0 \quad (39)$$

for the total charge density $\varrho = e_0(C + p - n + \rho_{\text{qd}} \operatorname{tr}(Z \boldsymbol{\rho}))$, where $\mathbf{J}_{\varrho} = e_0(\mathbf{J}_p - \mathbf{J}_n)$ is the electrical charge current density. For this (34), (35), (37) and cyclic permutations under the trace have been used. We conclude that the total charge $C(\boldsymbol{\rho}, n, p) = \int_{\Omega} \varrho \, dx$ is a conserved quantity.

The system (38) has a steady state solution $(\boldsymbol{\rho}, n, p) = (\boldsymbol{\rho}_{\text{eq}}, n_{\text{eq}}, p_{\text{eq}})$ where $[\boldsymbol{\rho}_{\text{eq}}, H] \equiv 0$ and $\mathfrak{D}_{\text{cp}}(n_{\text{eq}}) \boldsymbol{\rho}_{\text{eq}} \equiv 0$. Moreover, the steady state solution is assumed to satisfy

$$Q \boldsymbol{\rho}_{\text{eq}} = e^{-\beta \hbar \omega} \boldsymbol{\rho}_{\text{eq}} Q^*.$$

Then, the charge exchange (35) between the classical and the quantum system vanishes in equilibrium, i.e.,

$$R_n^{\text{quant-class}}(\boldsymbol{\rho}_{\text{eq}}, n_{\text{eq}}) = -\rho_{\text{qd}} \kappa(n_{\text{eq}}) \left(e^{\beta \hbar \omega / 2} \operatorname{tr}(Q \boldsymbol{\rho}_{\text{eq}} Q^*) - e^{-\beta \hbar \omega / 2} \operatorname{tr}(Q^* \boldsymbol{\rho}_{\text{eq}} Q) \right) = 0,$$

which is a manifestation of the detailed balance condition.

We consider the free energy functional $\mathcal{F}(\boldsymbol{\rho}, n, p)$ as given in (21) with the free energy density $F_{\text{carr}}(\mathbf{c}) = F_{\text{B}}(n, p)$ for the macroscopic carriers. The thermodynamic driving forces are obtained by the Gâteaux derivatives, namely

$$\begin{pmatrix} \boldsymbol{\sigma} \\ \mu_n \\ \mu_p \end{pmatrix} = \begin{pmatrix} D_{\boldsymbol{\rho}} \mathcal{F} \\ D_n \mathcal{F} \\ D_p \mathcal{F} \end{pmatrix} = \begin{pmatrix} E_{\beta} \log \boldsymbol{\rho} + H + e_0 \Phi_{\boldsymbol{\rho}, n, p} Z \\ E_{\beta} \log(n/n_{\text{eq}}) - e_0 \Phi_{\boldsymbol{\rho}, n, p} \\ E_{\beta} \log(p/p_{\text{eq}}) + e_0 \Phi_{\boldsymbol{\rho}, n, p} \end{pmatrix}.$$

Following [14] we consider solutions $t \mapsto (\boldsymbol{\rho}(t, \cdot), n(t, \cdot), p(t, \cdot))$ of (38) and discuss the energy-dissipation relation. A direct computation gives

$$\begin{aligned} \frac{d}{dt} \mathcal{F}(\boldsymbol{\rho}, n, p) &= \langle D\mathcal{F}(\boldsymbol{\rho}, n, p), (\dot{\boldsymbol{\rho}}, \dot{n}, \dot{p})^\top \rangle \\ &= -\mathcal{D}_{\text{transp}}(\boldsymbol{\rho}, n, p) - \mathcal{D}_{\text{react}}(\boldsymbol{\rho}, n, p) - \mathcal{D}_{\text{quant-class}}(\boldsymbol{\rho}, n, p) - \mathcal{D}_{\text{quant}}(\boldsymbol{\rho}, n, p), \end{aligned}$$

where we exploit the additive structure of the different dissipative mechanisms. Using (4), (5), (9), (34) and (37), the individual terms are given as follows:

$$\begin{aligned} \mathcal{D}_{\text{transp}} &= \int_{\Omega} \left(\frac{1}{e_0} \mathbb{M}_n n |\nabla (E_\beta \log(n/n_{\text{eq}}) - e_0 \Phi_{\boldsymbol{\rho}, n, p})|^2 \right. \\ &\quad \left. + \frac{1}{e_0} \mathbb{M}_p p |\nabla (E_\beta \log(p/p_{\text{eq}}) + e_0 \Phi_{\boldsymbol{\rho}, n, p})|^2 \right) dx, \\ \mathcal{D}_{\text{react}} &= E_\beta \int_{\Omega} r(n, p) \frac{(np - n_{\text{eq}} p_{\text{eq}})^2}{\Lambda(np, n_{\text{eq}} p_{\text{eq}})} dx, \\ \mathcal{D}_{\text{quant}} &= \int_{\Omega} \rho_{\text{qd}} \operatorname{tr} \left([-H - E_\beta \log \boldsymbol{\rho}] \mathfrak{D}_0 \boldsymbol{\rho} \right) dx, \\ \mathcal{D}_{\text{quant-class}} &= \int_{\Omega} \rho_{\text{qd}} \operatorname{tr} \left([-(H + E_\beta \log(n/n_{\text{eq}})Z) - \log \boldsymbol{\rho}] \mathfrak{D}_{\text{cp}}(q) \boldsymbol{\rho} \right) dx. \end{aligned}$$

Here, $\mathcal{D}_{\text{transp}}$ and $\mathcal{D}_{\text{react}}$, which describe the dissipation due to transport via drift and diffusion and due to reactions (recombination) in the van Roosbroeck system, are trivially non-negative. The non-negativity of $\mathcal{D}_{\text{quant}}$ follows from

$$\operatorname{tr} \left((\log \boldsymbol{\rho}_0 - \log \boldsymbol{\rho}) \mathfrak{D}_0 \boldsymbol{\rho} \right) \geq 0 \quad \text{for all } \boldsymbol{\rho} \in \mathfrak{R}_n, \quad (40)$$

whenever $\mathfrak{D}_0 \boldsymbol{\rho}_0 \equiv 0$, see [41, Thm. 3]. For the charge conserving processes this is easily achieved for $\log \boldsymbol{\rho}_0 = -\beta H$. The non-negativity of $\mathcal{D}_{\text{quant-class}}$ follows analogously by a generalization of (40) to

$$\operatorname{tr} \left((\log \widehat{\boldsymbol{\rho}}_n - \log \boldsymbol{\rho}) \mathfrak{D}_{\text{cp}}(n) \boldsymbol{\rho} \right) \geq 0 \quad \text{for all } \boldsymbol{\rho} \in \mathfrak{R}_n,$$

if $\mathfrak{D}_{\text{cp}}(n) \widehat{\boldsymbol{\rho}}_n \equiv 0$. Indeed, by (36) this is satisfied for $\log \widehat{\boldsymbol{\rho}}_n = -\beta H - \log(n/n_{\text{eq}})Z$. The proof is based on the relation $Q \widehat{\boldsymbol{\rho}}_n = e^{-(\beta \hbar \omega + \log(n/n_{\text{eq}}))} \widehat{\boldsymbol{\rho}}_n Q$. In conclusion, we recover the result of [14] and state consistency of the model system (38) with the second law of thermodynamics, as the free energy \mathcal{F} is a Liapunov function, namely $\frac{d}{dt} \mathcal{F}(\boldsymbol{\rho}, n, p) \leq 0$.

4.7 Quantum-classical coupling via Onsager operators

We can combine the ideas developed in Section 4.3 and Section 4.6 by looking at chemical reactions involving quantum states as well. For a single reaction we have

$$\widetilde{\alpha}_1 X_1 + \cdots + \widetilde{\alpha}_{i_*} X_{i_*} + \psi_j \rightleftharpoons \widetilde{\beta}_1 X_1 + \cdots + \widetilde{\beta}_{i_*} X_{i_*} + \psi_k \quad (41)$$

where $H\psi_j = h_j \psi_j$, $Z\psi_j = \zeta_j \psi_j$ and $[H, Z] = 0$. As before, the theory is based on coupling operators $Q_{j,k} = \psi_j \otimes \psi_k$ between the system's eigenstates that satisfy

$$[Q_{j,k}, H] = \hbar \omega_{j,k} Q_{j,k} \quad \text{and} \quad [Q_{j,k}, Z] = \ell_{j,k} Q_{j,k}, \quad (42)$$

with $\hbar\omega_{j,k} = h_k - h_j \neq 0$ and $\ell_{j,k} = \zeta_k - \zeta_j \in \mathbb{Z}$. We focus on a single reaction in (41) with (j, k) such that $\omega_{j,k} \equiv \omega_0$ and $\ell_{j,k} \equiv \ell_0$ such that charge conservation means

$$\mathbf{z} \cdot (\tilde{\boldsymbol{\beta}} - \tilde{\boldsymbol{\alpha}}) + \ell_0 = 0. \quad (43)$$

For example, the capture of an electron from the macroscopic system with $\mathbf{c} = (n, p)$ to the quantum system considered in Section 4.6 is described by $n + \psi_1 \rightleftharpoons \psi_2$, where, as in Section 4.6, ψ_1 models the empty quantum dot and ψ_2 is a state occupied by a single electron. The charge neutrality condition (43) is satisfied since $\mathbf{z} = (-1, +1)^\top$, $\tilde{\boldsymbol{\alpha}} = (1, 0)^\top$, $\tilde{\boldsymbol{\beta}} = (0, 0)^\top$ and $\ell_0 = -1$.

Following the general coupling strategy outlined in Section 3.4, we construct the coupling via a dual dissipation potential by using a suitable linear combination of the electro-chemical potential $\boldsymbol{\mu} = DF_{\text{carr}}(\mathbf{c}) + e_0\Phi_{\rho,\mathbf{c}}\mathbf{z}$ and the driving force $\boldsymbol{\sigma} = E_\beta \log \boldsymbol{\rho} + \mathbf{H} + e_0\Phi_{\rho,\mathbf{c}}\mathbf{Z}$. In particular, $\boldsymbol{\mu}$ is mapped into a multiple of the Hamiltonian \mathbf{H} or the charge operator \mathbf{Z} , such that it is possible to exploit the commutator relations (42) with the transition operator $Q_0 = Q_{j,k} = \psi_j \otimes \psi_k$. The dual dissipation potential reads

$$\mathcal{R}_{\text{quant-class}}^*(\boldsymbol{\rho}, \mathbf{c}; \boldsymbol{\sigma}, \boldsymbol{\mu}) := \beta \frac{\kappa(\mathbf{c})}{2} \text{tr} \left(([\mathbb{B}_{Q_0}, \mathbb{X}(\boldsymbol{\sigma} + \mathbf{A}\boldsymbol{\mu})])^* \mathfrak{C}_{R(\boldsymbol{\rho}, \gamma(\mathbf{c}))} [\mathbb{B}_{Q_0}, \mathbb{X}(\boldsymbol{\sigma} + \mathbf{A}\boldsymbol{\mu})] \right),$$

with $\mathbf{A}(\mathbf{c})\boldsymbol{\mu} := (\tilde{\boldsymbol{\beta}} - \tilde{\boldsymbol{\alpha}}) \cdot \boldsymbol{\mu} (a(\mathbf{c})\mathbf{H} + b(\mathbf{c})\mathbf{Z}) \in \mathbb{C}_{\text{Herm}}^{n \times n}$,

where the coupling strength $\kappa(\mathbf{c}) \geq 0$ will remain free, while the scalars $a(\mathbf{c})$, $b(\mathbf{c})$, and $\gamma(\mathbf{c})$ need to be chosen suitably as functions of \mathbf{c} to be able to exploit electro-neutrality and the generalized miracle identity (32) for all \mathbf{c} . For this, we simply observe that replacing \mathbf{H} by $b(\mathbf{c})\mathbf{H}$ does not change Q_0 , but replaces ω_0 by $b(\mathbf{c})\omega_0$. Thus, with $(\boldsymbol{\sigma}, \boldsymbol{\mu}) = (E_\beta \log \boldsymbol{\rho} + \mathbf{H} + e_0\Phi_{\rho,\mathbf{c}}\mathbf{Z}, DF_{\text{carr}}(\mathbf{c}) + e_0\Phi_{\rho,\mathbf{c}}\mathbf{z})$ we obtain the commutator relation

$$\begin{aligned} [Q_0, \boldsymbol{\sigma} + \mathbf{A}(\mathbf{c})\boldsymbol{\mu}] &= E_\beta [Q_0, \log \boldsymbol{\rho}] + E_\beta \gamma(\mathbf{c}, \Phi_{\rho,\mathbf{c}}) Q_0 \quad \text{with} \\ \gamma(\mathbf{c}, \Phi_{\rho,\mathbf{c}}) &= \beta \left(\hbar\omega_0 + (\tilde{\boldsymbol{\beta}} - \tilde{\boldsymbol{\alpha}}) \cdot (DF_{\text{carr}}(\mathbf{c}) (\hbar\omega_0 a(\mathbf{c}) + \ell_0 b(\mathbf{c})) \right. \\ &\quad \left. + e_0\Phi_{\rho,\mathbf{c}} (\ell_0 + (\tilde{\boldsymbol{\beta}} - \tilde{\boldsymbol{\alpha}}) \cdot \mathbf{z} (\hbar\omega_0 a(\mathbf{c}) + \ell_0 b(\mathbf{c}))) \right). \end{aligned}$$

Thus, to have electro-neutrality (43) the factor multiplying $e_0\Phi_{\rho,\mathbf{c}}$ has to vanish, which by (43) imposes the condition $\hbar\omega_0 a(\mathbf{c}) + \ell_0 b(\mathbf{c}) \equiv 1$. (For the case treated in Section 4.6 a natural choice is $a(n, p) \equiv 0$ and $b(n, p) = 1/\ell_0 = -1$.) Moreover, we find that γ does not depend on $\Phi_{\rho,\mathbf{c}}$ and takes the simple form

$$\gamma(\mathbf{c}) = \beta \hbar\omega_0 + \beta (\tilde{\boldsymbol{\beta}} - \tilde{\boldsymbol{\alpha}}) \cdot DF_{\text{carr}}(\mathbf{c}). \quad (44)$$

The associated Onsager operator now has a block structure

$$\mathbb{K}_{\text{quant-class}}(\boldsymbol{\rho}, \mathbf{c}) = \kappa(\mathbf{c}) \begin{pmatrix} \mathbb{K}_{\text{quant}}^{\text{cq}}(\boldsymbol{\rho}, \mathbf{c}) & \mathbb{K}_{\text{quant}}^{\text{cq}}(\boldsymbol{\rho}, \mathbf{c}) \mathbf{A}(\mathbf{c}) \\ \mathbf{A}^*(\mathbf{c}) \mathbb{K}_{\text{quant}}^{\text{cq}}(\boldsymbol{\rho}, \mathbf{c}) & \mathbf{A}^*(\mathbf{c}) \mathbb{K}_{\text{quant}}^{\text{cq}}(\boldsymbol{\rho}, \mathbf{c}) \mathbf{A}(\mathbf{c}) \end{pmatrix}$$

that clearly shows the symmetric coupling. Here $\mathbb{K}_{\text{quant}}^{\text{cq}}$ is constructed as in (33), namely

$$\mathbb{K}_{\text{quant}}(\boldsymbol{\rho}, \mathbf{c}) \boldsymbol{\sigma} = -\beta \kappa(\mathbf{c}) \mathbb{X}^* \left[\mathbb{B}_{Q_0}, \mathfrak{C}_{R(\boldsymbol{\rho}, \gamma(\mathbf{c}))} [\mathbb{B}_{Q_0}, \mathbb{X} \boldsymbol{\sigma}] \right], \quad (45)$$

where now an explicit dependence on the macroscopic densities c_i occurs.

It is interesting to note that this construction yields a simple final result for the coupling terms in the equations if we use Maxwell–Boltzmann statistics for \mathbf{c} , because the arising terms for the macroscopic system are very similar to the expressions for the quantum system that are based on the von Neumann entropy.

Using coupling strength function $\kappa(\mathbf{c}) = \kappa_0(\tilde{\mathbf{c}}^{\tilde{\alpha}}\tilde{\mathbf{c}}^{\tilde{\beta}})^{1/2}$ (which also occurs in [27], see (27)), we obtain

$$\begin{aligned} \begin{pmatrix} \mathcal{D}_{\text{quant-class}}(\mathbf{c})\boldsymbol{\rho} \\ -\mathbf{R}_{\text{quant-class}}(\boldsymbol{\rho}, \mathbf{c}) \end{pmatrix} &= -\mathbb{K}_{\text{qu-cl}}(\boldsymbol{\rho}, \mathbf{c}) \begin{pmatrix} E_{\beta} \log \boldsymbol{\rho} + H + e_0 \Phi_{\boldsymbol{\rho}, \mathbf{c}} Z \\ DF_{\mathbf{B}}(\mathbf{c}) + e_0 \Phi_{\boldsymbol{\rho}, \mathbf{c}} \mathbf{z} \end{pmatrix} \\ &= \kappa_0 \begin{pmatrix} e^{\beta \hbar \omega_0 / 2} \tilde{\mathbf{c}}^{\tilde{\alpha}} \mathbb{G}_{Q_0} \boldsymbol{\rho} + e^{-\beta \hbar \omega_0 / 2} \tilde{\mathbf{c}}^{\tilde{\beta}} \mathbb{G}_{Q_0^*} \boldsymbol{\rho} \\ (e^{\beta \hbar \omega_0 / 2} \tilde{\mathbf{c}}^{\tilde{\alpha}} \text{tr}(Q_0 \boldsymbol{\rho} Q_0^*) - e^{-\beta \hbar \omega_0 / 2} \tilde{\mathbf{c}}^{\tilde{\beta}} \text{tr}(Q_0^* \boldsymbol{\rho} Q_0)) (\tilde{\alpha} - \tilde{\beta}) \end{pmatrix}, \end{aligned} \quad (46)$$

where $\tilde{\mathbf{c}} = (c_i / c_i^{\text{eq}})_{i=1, \dots, i_*}$ is the vector of relative densities. It is surprising that all the terms are polynomial in \mathbf{c} and linear in $\boldsymbol{\rho}$. We refer to (35) and (38) in Section 4.6 for the special case with $\tilde{\alpha} = (1, 0)^{\top}$ and $\tilde{\beta} = (0, 0)^{\top}$.

The surprising fact is that by the generalized miracle identity (32) all the complicated nonlinearity cancels each other, and at the end polynomial vector fields remain. In particular the equation for $\boldsymbol{\rho}$ is in Lindblad form, where only the prefactors of the generators \mathbb{G}_{Q_0} and $\mathbb{G}_{Q_0^*}$ depend on the macroscopic charge carrier densities. Similarly, the reactions of the charge carrier densities c_i obey the mass-action law, see (26). We refer to [26, 12] for more details concerning the coupling of charge carriers and quantum systems.

4.8 Further dissipative coupling strategies

Further dissipative processes can be modeled by similar approaches. For instance, in [29, Sec. 5.5] a dissipative Maxwell–Bloch system is considered, where a dissipative coupling between the electromagnetic radiation field and a quantum mechanical multi-level system is considered. A much simpler and more direct coupling of recombination and light generation is discussed in [28]. In [11] a different model for dissipative Maxwell equations is formulated within the framework of GENERIC.

Many applications involve the interaction of bulk and interface effects. We refer to [32, 7, 24]. In particular, the capture and escape of species from the bulk to the interface and back can be understood as a reaction in the sense of Section 4.3.

References

- [1] Albinus, G., Gajewski, H., Hünlich, R.: Thermodynamic design of energy models of semiconductor devices. *Nonlinearity* **15**(2), 367–383 (2002). DOI 10.1088/0951-7715/15/2/307
- [2] Bimberg, D., Grundmann, M., Ledentsov, N.N.: Quantum Dot Heterostructures. John Wiley & Sons, Chichester (1999)
- [3] Bloch, A.M., Morrison, P.J., Ratiu, T.S.: Gradient flows in the normal and Kähler metrics and triple bracket generated metriplectic systems. In: A. Johann, H.P. Kruse, F. Rupp,

- S. Schmitz (eds.) *Recent Trends in Dynamical Systems*, chap. 15, pp. 371–415. Springer, Basel, Heidelberg (2013). DOI 10.1007/978-3-0348-0451-6_15
- [4] Breuer, H.P., Petruccione, F.: *The Theory of Open Quantum Systems*. Oxford University Press, Oxford (2002). DOI 10.1093/acprof:oso/9780199213900.001.0001
- [5] Carlen, E.A., Maas, J.: Gradient flow and entropy inequalities for quantum Markov semi-groups with detailed balance. *J. Funct. Analysis* **273**(5), 1810–1869 (2017). DOI 10.1016/j.jfa.2017.05.003
- [6] Chow, W.W., Jahnke, F.: On the physics of semiconductor quantum dots for applications in lasers and quantum optics. *Prog. Quantum Electron.* **37**(3), 109–184 (2013). DOI 10.1016/j.pquantelec.2013.04.001
- [7] Glitzky, A., Mielke, A.: A gradient structure for systems coupling reaction-diffusion effects in bulk and interfaces. *Z. angew. Math. Phys. (ZAMP)* **64**, 29–52 (2013). DOI 10.1007/s00033-0012-207-y
- [8] Grmela, M.: Multiscale equilibrium and nonequilibrium thermodynamics in chemical engineering. *Adv. Chem. Eng.* **39**, 75–128 (2010). DOI 10.1016/s0065-2377(10)39002-8
- [9] Grmela, M., Öttinger, H.C.: Dynamics and thermodynamics of complex fluids. I. Development of a general formalism. *Phys. Rev. E* **56**(6), 6620–6632 (1997). DOI 10.1103/physreve.56.6620
- [10] de Groot, S.R., Mazur, P.: *Non-equilibrium thermodynamics*. North-Holland Publishing, Amsterdam (1962)
- [11] Jelić, A., Hütter, M., Öttinger, H.C.: Dissipative electromagnetism from a nonequilibrium thermodynamics perspective. *Phys. Rev. E* **74**, 041126 (2006). DOI 10.1103/physreve.74.041126
- [12] Kantner, M.: *Modeling and simulation of electrically driven quantum dot based single-photon sources: From classical device physics to open quantum systems*. Ph.D. thesis, Technical University Berlin, Berlin (2018). DOI 10.14279/depositonce-7516
- [13] Kantner, M., Bandelow, U., Koprucki, T., Schulze, J.H., Strittmatter, A., Wünsche, H.J.: Efficient current injection into single quantum dots through oxide-confined pn-diodes. *IEEE Trans. Electron Devices* **63**, 2036–2042 (2016). DOI 10.1109/ted.2016.2538561
- [14] Kantner, M., Mittnenzweig, M., Koprucki, T.: Hybrid quantum-classical modeling of quantum dot devices. *Phys. Rev. B* **96**, 205301/1–17 (2017). DOI 10.1103/PhysRevB.96.205301
- [15] Koprucki, T., Gärtner, K.: Discretization scheme for drift-diffusion equations with strong diffusion enhancement. *Opt. Quant. Electron.* **45**(7), 791–796 (2013). DOI 10.1007/s11082-013-9673-5
- [16] Kubo, R.: Some aspects of the statistical-mechanical theory of irreversible processes. In: W.E. Brittin, L.G. Dunham (eds.) *Lectures in Theoretical Physics*. Interscience Publishers, New York (1959)

- [17] Liero, M., Mielke, A., Peletier, M.A., Renger, D.R.M.: On microscopic origins of generalized gradient structures. *Discr. Cont. Dynam. Systems Ser. S* **10**(1), 1–35 (2017). DOI 10.3934/dcdss.2017001
- [18] Lindblad, G.: Completely positive maps and entropy inequalities. *Comm. Math. Phys.* **40**, 147–151 (1975). DOI 10.1007/BF01609396
- [19] Lindblad, G.: On the generators of quantum dynamical semigroups. *Comm. Math. Phys.* **48**(2), 119–130 (1976)
- [20] Markowich, P.A.: *The Stationary Semiconductor Device Equations*. Springer, Wien, New York (1986). DOI 10.1007/978-3-7091-3678-2
- [21] van Mensfoort, S.L.M., Coehoorn, R.: Effect of Gaussian disorder on the voltage dependence of the current density in sandwich-type devices based on organic semiconductors. *Phys. Rev. B* **78**(8), 085207 (2008). DOI 10.1103/PhysRevB.78.085207
- [22] Mielke, A.: Formulation of thermoelastic dissipative material behavior using GENERIC. *Contin. Mech. Thermodyn.* **23**(3), 233–256 (2011). DOI 10.1007/s00161-010-0179-0
- [23] Mielke, A.: A gradient structure for reaction-diffusion systems and for energy-drift-diffusion systems. *Nonlinearity* **24**, 1329–1346 (2011). DOI 10.1088/0951-7715/24/4/016
- [24] Mielke, A.: Thermomechanical modeling of energy-reaction-diffusion systems, including bulk-interface interactions. *Discr. Cont. Dynam. Systems Ser. S* **6**(2), 479–499 (2013). DOI 10.3934/dcdss.2013.6.479
- [25] Mielke, A.: On thermodynamical couplings of quantum mechanics and macroscopic systems. In: P. Exner, W. König, H. Neidhardt (eds.) *Mathematical Results in Quantum Mechanics*, pp. 331–348. World Scientific, Singapore (2015). *Proceedings of the QMath12 Conference*
- [26] Mielke, A., Mittnenzweig, M., Rotundo, N.: On a thermodynamically consistent coupling of quantum systems to reaction-rate equation. In preparation (2017)
- [27] Mielke, A., Patterson, R.I.A., Peletier, M.A., Renger, D.R.M.: Non-equilibrium thermodynamical principles for chemical reactions with mass-action kinetics. *SIAM J. Appl. Math.* **77**(4), 1562–1585 (2017). DOI 10.1137/16M1102240
- [28] Mielke, A., Peschka, D., Rotundo, N., Thomas, M.: On some extension of energy-drift-diffusion models: Gradient structures for optoelectronic models of semiconductors. In: P. Quintela, P. Barral, D. Gómez, F.J. Pena, J. Rodríguez, P. Salgado, M. Vázquez-Méndez (eds.) *Progress in Industrial Mathematics at ECMI 2016, Mathematics in Industry Vol. 26*, pp. 291–298. Springer (2017). DOI 10.1007/978-3-319-63082-3_45
- [29] Mittnenzweig, M., Mielke, A.: An entropic gradient structure for Lindblad equations and couplings of quantum systems to macroscopic models. *J. Stat. Phys.* **167**(2), 205–233 (2017). DOI 10.1007/s10955-017-1756-4
- [30] Morrison, P.J.: A paradigm for joined Hamiltonian and dissipative systems. *Phys. D* **18**(1-3), 410–419 (1986)

- [31] Onsager, L.: Reciprocal relations in irreversible processes, I. *Phys. Rev.* **37**, 405–426 (1931). DOI 10.1103/PhysRev.37.405
- [32] Öttinger, H.C.: Nonequilibrium thermodynamics for open systems. *Phys. Rev. E* **73**(3), 036126 (2006). DOI 10.1103/physreve.73.036126
- [33] Öttinger, H.C.: The nonlinear thermodynamic quantum master equation. *Phys. Rev. A* **82**, 052119 (2010)
- [34] Öttinger, H.C.: The geometry and thermodynamics of dissipative quantum systems. *Europhys. Lett.* **94**, 10006 (2011). DOI 10.1209/0295-5075/94/10006
- [35] Öttinger, H.C., Grmela, M.: Dynamics and thermodynamics of complex fluids. II. Illustrations of a general formalism. *Phys. Rev. E* **56**(6), 6633–6655 (1997)
- [36] Palankovski, V., Quay, R.: *Analysis and Simulation of Heterostructure Devices. Computational Microelectronics.* Springer Science & Business Media, Vienna (2004). DOI 10.1007/978-3-7091-0560-3
- [37] Paul, H.: *Photonen: Eine Einführung in die Quantenoptik.* Vieweg+Teubner Verlag, Stuttgart, Leipzig (1995). DOI 10.1007/978-3-322-96700-8
- [38] van Roosbroeck, W.: Theory of the flow of electrons and holes in germanium and other semiconductors. *Bell Syst. Tech. J.* **29**(4), 560–607 (1950). DOI 10.1002/j.1538-7305.1950.tb03653.x
- [39] Schröder, D.: *Modelling of interface carrier transport for device simulation. Series in Computational Microelectronics.* Springer, Vienna (1994). DOI 10.1007/978-3-7091-6644-4
- [40] Selberherr, S.: *Analysis and simulation of semiconductor devices.* Springer, Wien, New York (1984). DOI 10.1007/978-3-7091-8752-4
- [41] Spohn, H.: Entropy production for quantum dynamical semigroups. *J. Math. Phys.* **19**(5), 1227–1230 (1978). DOI 10.1063/1.523789
- [42] Spohn, H., Lebowitz, J.L.: Irreversible thermodynamics for quantum systems weakly coupled to thermal reservoirs. *Adv. Chemical Physics XXXVIII* pp. 109–142 (1978). DOI 10.1002/9780470142578.ch2
- [43] Weiss, U.: *Quantum Dissipative Systems*, 2nd edn. World Scientific, Singapore (1999). DOI 10.1142/6738
- [44] Wilcox, R.M.: Exponential operators and parameter differentiation in quantum physics. *J. Math. Phys.* **8**(4), 962–982 (1967). DOI 10.1063/1.1705306
- [45] Yong, W.A.: An interesting class of partial differential equations. *J. Math. Phys.* **49**, 033503, 21 (2008). DOI 10.1063/1.2884710